



Optimization of Ammonium Sulfamate Nitration for the Preparation of Ammonium Dinitramide

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Abstract: The reaction kinetics for the preparation of ammonium dinitramide (ADN) is described. ADN is the ammonium salt of the dinitramide anion, and belongs to the group of inorganic oxidizers, mainly useful for energetic rocket propellant formulations, particularly for underwater applications. It is also a potential candidate to replace ammonium perchlorate (AP), in order to develop chlorine-free, green propellants. At HEMRL, ADN is prepared by the nitration of ammonium sulfamate (AS) using mixed acid, followed by hydrolysis, neutralization with ammonia (g) and rectification using solvent. The nitration of ammonium sulfamate (AS) is carried out at a subzero temperature of -40 ± 1 °C. The yield of ADN is reliant on the formation of dinitramidic acid, an intermediate product formed during the hydrolysis step, and its stability is predominantly dependent upon the level of acidity and temperature of the reaction medium. Prior to these kinetics studies, process optimization of the nitration of ammonium sulfamate (AS) was performed and gave the final mole ratio of $AS:HNO_3:H_2SO_4$. Since the nitration of AS is sensitive to temperature, the rate of reaction was studied at fixed temperatures with variation of time, keeping all of the other parameters, such as vessel volume, agitator speed, feed rate *etc.*, constant. During these studies, predetermined quantities of ammonium sulfamate (AS) and mixed acid were allowed to react at a fixed temperature (-40 ± 1 °C) for different reaction periods

to generate the concentration profile of AS. Using this concentration profile, the reaction order and reaction rate constant were evaluated. In order to find the effect of temperature on the reaction rate and yield, experiments were conducted at other temperatures such as -30 and -50 °C. In the present studies, it was found that the optimum temperature of nitration is -40 ± 1 °C and that the rate of reaction follows a pseudo second order process with rate constant $0.01113 \text{ (min}^{-1}) \cdot (\text{mol/L})^{-1}$. The reaction time evaluated for 55 to 60% conversion is about 70-80 minutes at -40 ± 1 °C, based on this kinetics. The activation energy of AS nitration was found to be -4.6 kcal/mol, using the reaction kinetic data based on the temperature dependent rate equation derived from Arrhenius's law.

1 Introduction

Ammonium dinitramide (ADN), an environmental-friendly compound, has been of considerable interest in the recent years. Generally, ammonium perchlorate (AP) is the common, widely used oxidizer in composite solid propellants. The disadvantage of AP is that its chlorinated exhaust products are detrimental to the environment and produce a distinct signature behind missiles that can be easily detected [1]. Various authors [2-4] have reported their views about the health/environmental issues when using AP in propellant formulations. According to their reports, AP may cause thyroid cancer by contaminating soil and water. Also, AP produces a lot of hydrogen chloride (HCl (g)) during the burning of the propellant, which can cause high concentrations of acid rain and depletion of the ozone layer. In view of this, growing environmental awareness has generated an interest in research for new, environmentally friendly, high performance oxidizers like ADN. ADN is a chlorine-free inorganic oxidizer with minimum signature characteristics, as well as giving no hydrochloric acid production from commercial solid rocket propellants, therefore it is considered as a potential candidate for replacement of AP in composite propellant formulations. In addition to the reduction in the level of harmful contaminants introduced to the environment, the weight of the rocket motor is expected to be reduced by about 40%, with the specific impulse being enhanced by 20% [5]. Thus, ADN has created significant interest in recent years. However, the synthesis of highly energetic, halogen-free materials like ADN in high yield and purity is one of the challenging tasks. Russian scientists at the Zelinsky Institute of Russia invented a method for synthesizing the dinitramide anion [6-7] in 1971. Later Bottaro [8] and co-workers in USA developed methods for the synthesis of both inorganic and organic dinitramide by the nitration of nitramide (NH_2NO_2) using nitronium tetrafluoroborate (NO_2BF_4) and dinitrogen pent oxide (N_2O_5). The yields varied

from 1% to 35%. Hatano and co-workers [9] reported a clean and safe method for making ammonium dinitramide from urea using HNO_3 , NO_2BF_4 and liquid NH_3 , in 5 to 20% yield. Stern *et al.* [10] prepared ammonium dinitramide in 50 to 60% yield from ethyl- or methyl-N-nitrocarbamate by ammonia treatment followed by nitration. Ethyl- or methyl-N-nitrocarbamate had to be prepared initially by the nitration of ethyl or methyl carbonate respectively using acetic anhydride (Ac_2O) and HNO_3 . Langlet *et al.* [11] synthesized ADN in 60% yield by the nitration of ammonium sulfamate derivatives like $\text{NH}_4\text{SO}_3\text{NH}_2$ and $\text{NH}(\text{SO}_3\text{NH}_4)_2$ using mixed acid (fuming H_2SO_4 /fuming HNO_3). At the High Energy Materials Research Laboratory (HEMRL), ADN is prepared by a batch process involving nitration of ammonium sulfamate (AS) using a nitrating mixture of concentrated nitric and concentrated sulfuric acid. However, no literature is available on the reaction kinetics and optimization, hence a study was undertaken to determine these for the nitration of AS, optimization of the reaction parameters, the temperature dependent rate equation *etc.* The kinetics of the overall reaction is basically a study of the slowest step [12-14]. The study was carried out at different temperatures, keeping other parameters constant. A subzero reaction temperature was maintained using a dry ice/acetone bath. During these studies, predetermined optimized quantities of AS and mixed acid were allowed to react at a fixed temperature for different reaction periods to generate a concentration profile of the reactant. Using this concentration profile, the reaction order and reaction rate constant were evaluated. Three sets of experiments were conducted to optimize the reaction temperature and also to find the temperature dependent rate equation. The activation energy was evaluated using the temperature dependent rate constants.

2 Experimental

2.1 Reaction Procedure

The nitration of AS is a hazardous, heterogeneous reaction showing little exothermicity, which is essentially required to be carried out at sub-zero temperatures, where a mixture of concentrated sulphuric acid, H_2SO_4 (98%), and nitric acid, HNO_3 (98%), is used as the nitrating agent. Vacuum dried, finely ground, free flowing ammonium sulfamate (AS) was added, with continuous stirring during 10-15 minutes, to the mixed acid in the mole ratios of $\text{AS}:\text{HNO}_3:\text{H}_2\text{SO}_4 :: 1:16:2.7$ and the temperature was maintained at the desired level. The AS nitration, the reaction relevant to present experimental work, is shown in Figure 1.

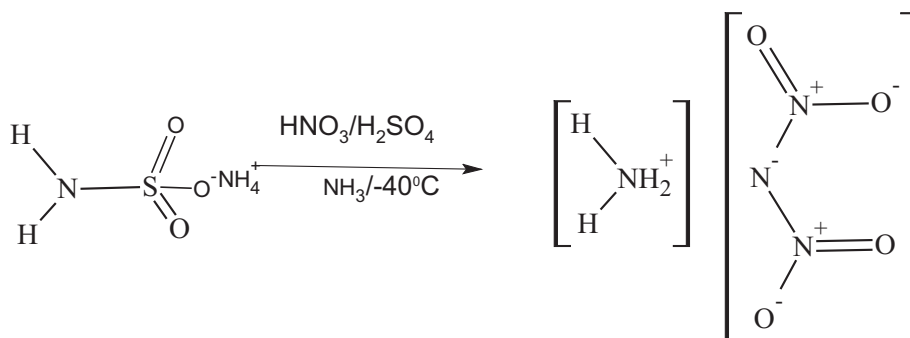


Figure 1. The chemistry of ADN preparation.

2.2 Experimental

The experimental set-up (Figure 2) consisted of a three-necked, round bottomed flask (1000 mL, used as the reactor) fitted with a driving motor, agitator, temperature sensors/indicators in the reactor as well as in the cooling bath. Dry ice and acetone in the bath were used to maintain the desired reaction temperature. In order to optimize the reaction temperature and to determine the temperature dependent rate constant, three sets of experiments were conducted at -50, -40 and -30 °C. For each temperature, a number of experiments were carried out for reaction times ranging from 15 to 120 minutes. After the required reaction time, crushed ice was added to the reaction mixture. Ammonia gas was then bubbled into the reaction mixture until the pH of the mixture reached to 7-11. The reaction mixture was allowed to settle for some time before the white solid bi-product was separated by filtration. The filtrate (aqueous part) was evaporated to dryness to produce a semi-solid mass. Propan-2-ol (~400 mL) was then added to the semi-solid mass in order to remove traces of water and to obtain a dry, free-flowing powder. The same process was repeated once more to ensure that the final traces of water had been removed. The solid mass was then extracted with boiling ethyl acetate (~300 mL), in which the ADN dissolves. The extraction was repeated two or three times to extract the ADN completely from the solid mass. The combined ethyl acetate fractions were evaporated to obtain crude ADN (off-white in colour, purity ~90%, m.p. ~88 °C). Recrystallization of the crude ADN was carried out with boiling ethyl acetate, which gives ADN of purity greater than 98%, m.p. ~92 °C. The product (ADN) weight was determined for each run after drying and the melting point was noted. The conversion of AS to ADN at different temperatures was recorded and plotted. The reaction rates and activation energy were calculated on the basis of these data.



Figure 2. Schematic diagram of the laboratory set-up for ADN preparation at HEMRL:

1 – reaction bath, 2 – ammonia gas line, 3 – reactor, 4 – mechanical agitator, 5 – rotary film evaporator, 6 – temp. indicator, 7 – fume trap, 8 – condenser, 9 – collection vessel, 10 – heater.

3 Analysis of Kinetic Data

3.1 Reaction rate

Several methods are available for determining the order of the reaction and subsequently the rate law of the chemical reaction. These [12, 13] are mainly the integral method, the differential method, the method of half-life, the isolation method, the method of excess *etc.* As the nitration of AS is sensitive to temperature, the rate of reaction was studied at fixed temperatures with variation of time, keeping all other parameters constant. In each method, it is essential to estimate the concentration of the reactant or the product at different reaction times. In the present study, differential method was adopted to determine the rate law for this reaction. Hence, the reaction rate (r) can be expressed as:

$$-r = k \cdot (C_{AS})^n \cdot (C_{HNO_3})^m \quad (1)$$

where k is the reaction rate constant, m and n are orders of reaction with respect to HNO_3 and AS respectively. Using the concentration profiles (Figures 3-7) of AS and HNO_3 at different temperatures, it is seen that the change of nitric acid concentration (Figure 7) is almost negligible compared to that of AS. So the

overall rate of the reaction can be written as:

$$-r_B = -\frac{dC_B}{dt} = k \cdot (C_B)^n \quad (2)$$

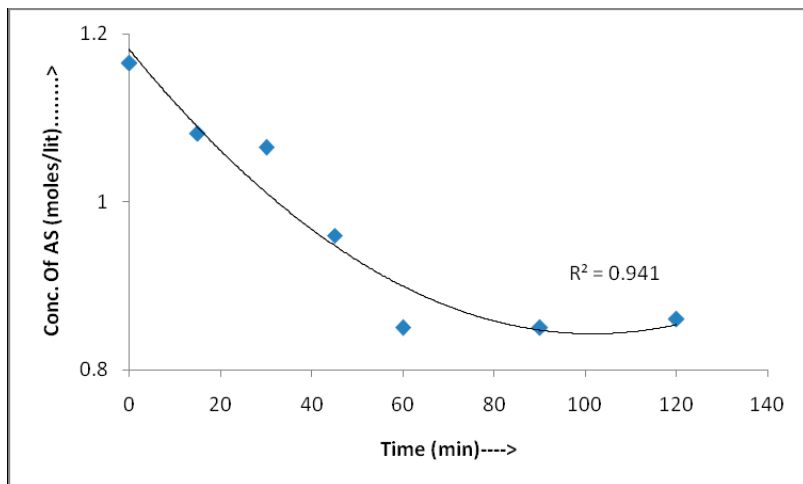


Figure 3. Variation of the concentration of AS at -50 °C.

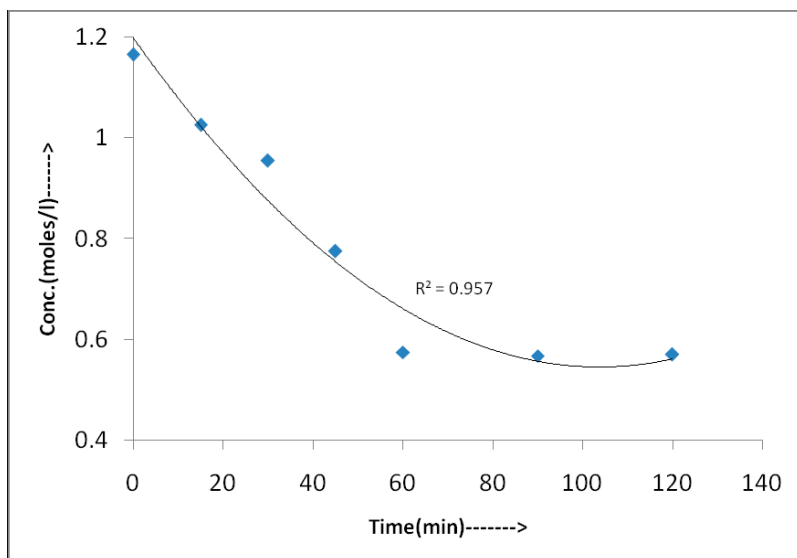


Figure 4. Variation of the concentration of AS at -40 °C.

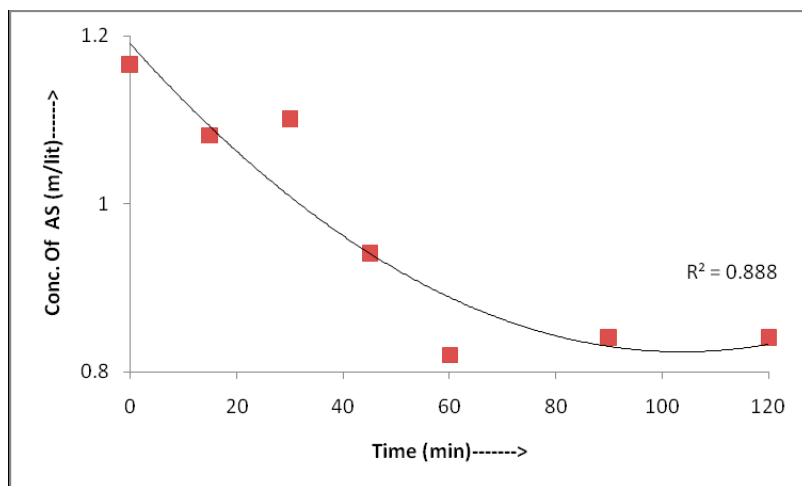


Figure 5. Variation of the concentration AS at -30 °C.

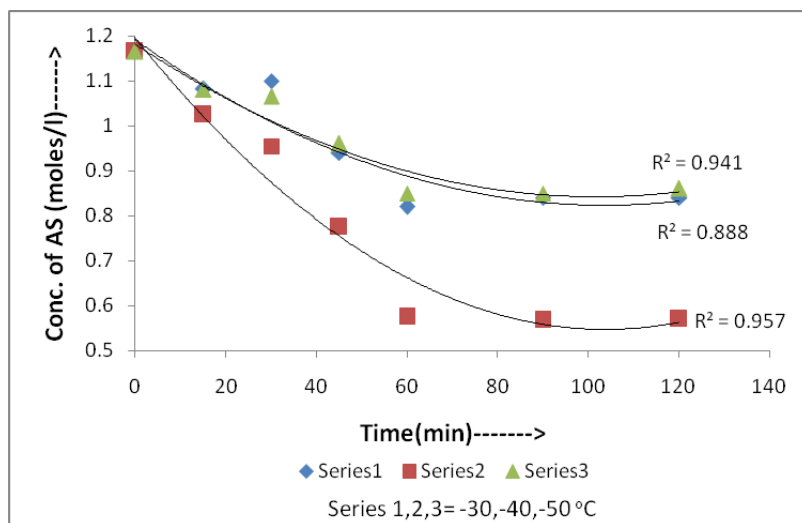


Figure 6. Variation of the concentration AS at -30, -40 and -50 °C.

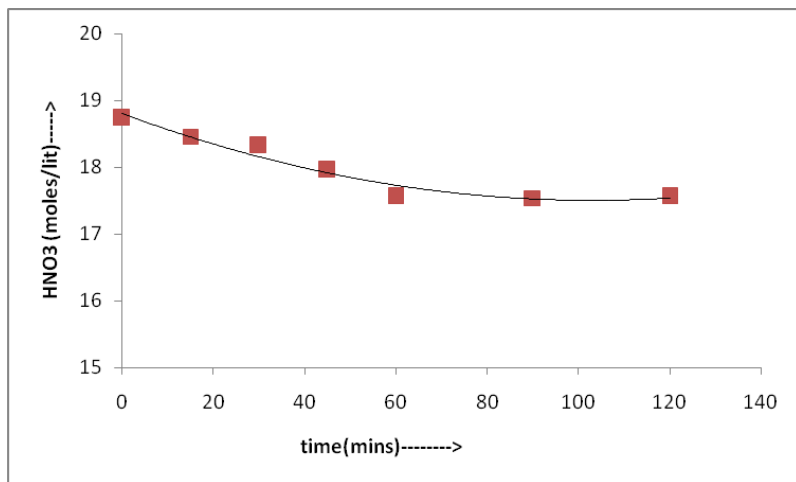


Figure 7. Variation of HNO₃ concentration at -40 °C.

Here, n is the order of the reaction, and C_B is the concentration of AS. Taking natural logarithms (\ln) of both sides of the equation, (2) can be written as:

$$\ln\left(-\frac{dC_B}{dt}\right) = \ln(k) + n \ln(C_B) \quad (3)$$

From the experimental data, a plot of the concentration (C_B) vs. time (t) for the depletion of AS was obtained. The slopes of the curves in Figures 3-6 are $\left(\frac{dC_B}{dt}\right)$. Thus, the order, n and the rate constant, k can be found from a plot of $\ln(C_B)$ vs. $\ln\left(-\frac{dC_B}{dt}\right)$. By integrating Eq. (2), the reaction time for any amount

of conversion can be calculated as shown below:

$$\text{Case-I: } n \neq 1, \quad t = \left(\frac{1}{k}\right) \left[\frac{C_B^{1-n}}{1-n} \right]_{C_{Bi}}^{C_{Bf}} \quad (4)$$

$$\text{Case-II: } n = 1, \quad t = \left(\frac{1}{k}\right) \ln \left[\frac{C_{Bf}}{C_{Bi}} \right] \quad (5)$$

where t is the reaction time, and C_{Bi} and C_{Bf} are the initial and final concentrations of B.

3.2 Temperature dependency rate equation

The kinetics of the above reaction has been measured at 3 different temperatures -50, -40 and -30 °C. As the temperature increases, the rate constant (k) increases from -50 to -40 °C, however it decreases from -40 to -30 °C, without altering the reaction order. Reactions exhibiting this kind of trend are typically reactions where the progress of the reaction depends upon the capture of the molecule in a potential well. Increasing the temperature may lead to a reduced probability of molecules colliding with more glancing collisions and does not lead to reaction due to a higher momentum, which generally leads to the colliding particles moving out of the potential well. Using the values of k at different temperatures, the temperature dependency rate equation was derived using Arrhenius's law as follows:

$$k = k_0 e^{-E/RT} \quad (6)$$

where k_0 is called the frequency factor, E is the activation energy of the reaction and R is the universal gas constant. Taking natural logarithms of both sides of Eq. (6), it can be written as:

$$\ln(k) = \ln(k_0) - \left(\frac{E}{R}\right) \cdot \frac{1}{T} \quad (7)$$

The rate equation is obtained from a plot of $\ln\left(-\frac{dC_B}{dt}\right)$ vs. $\ln(C_B)$, as shown in Figure 8. The reaction rate constants (k) are evaluated from the rate equations and the reaction rate equations at different temperatures are tabulated and shown in Table 1. The temperature dependency rate expression, k as $f(T)$ can be evaluated from the graph as shown in Figure 9.

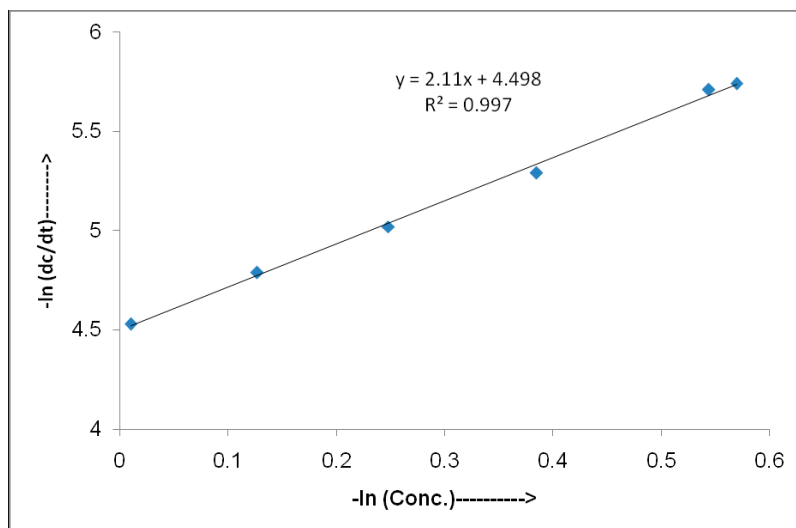


Figure 8. Reaction rate equation at $-40\text{ }^{\circ}\text{C}$.

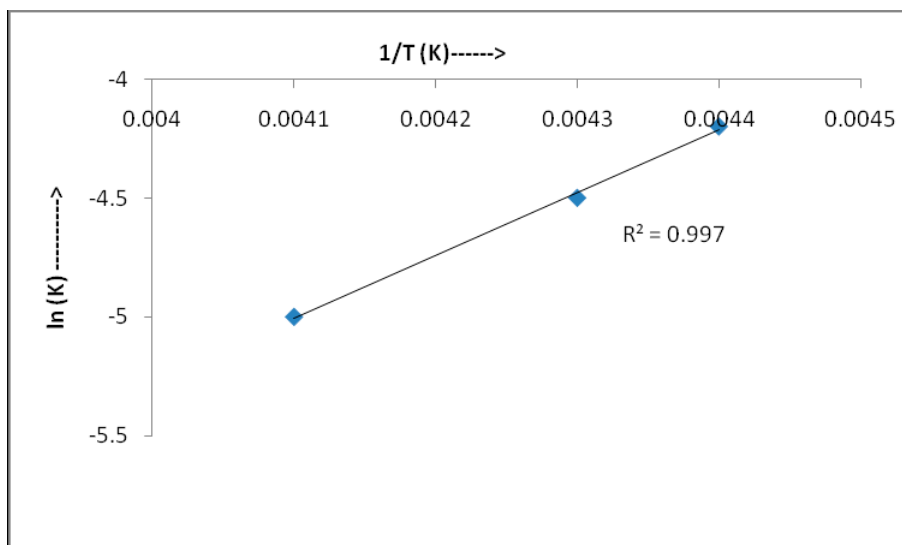


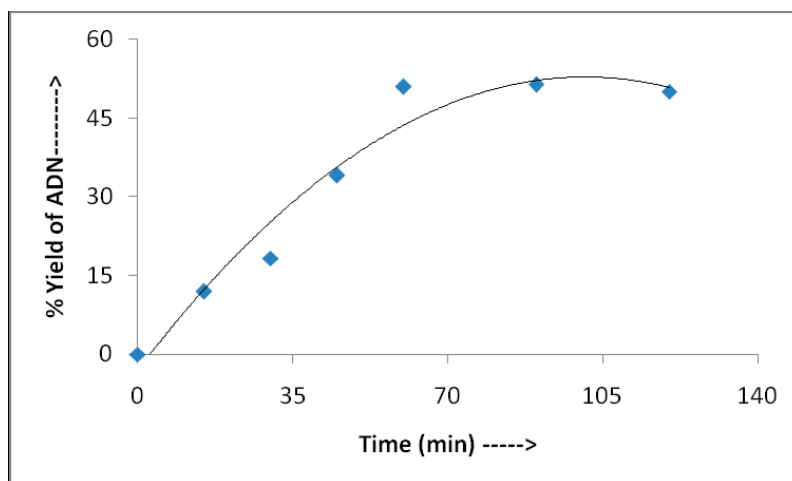
Figure 9. Temperature dependency rate equation according to Arrhenius's law.

Table 1. Nitration rate equations from the kinetic studies

Sl. No.	Temperature (°C)	Rate equations	Pseudo reaction order, n	Pseudo reaction rate constant, k (mol/L) ⁻¹ ·(min) ⁻¹
1	-50	$\frac{dC_B}{dt} = -0.00607 C_B^{2.1}$	~2	0.00607
2	-40	$\frac{dC_B}{dt} = -0.01113 C_B^{2.1}$		0.01113
3	-30	$\frac{dC_B}{dt} = -0.006849 C_B^{2.1}$		0.006849

3.3 Optimization of the reaction parameters

Nitration's of AS were carried out in a wide temperature domain, ranging from -50 to -30 °C, where the reaction takes place at a reasonable rate. During the reaction, hazardous intermediate products like dinitramidic acid form which decompose at higher temperatures thereby decrease the yield of the product ADN. Hence, it is essential to know the lowest possible operating temperature at which the reaction generates the maximum yield and the optimum heat generation rate during the process. Figure 10 shows the yield (%) of ADN with time, Figure 11 shows the yield of ADN against moles of nitric acid, and Figure 12 shows the yield of ADN against temperature. Comparing Figures 10-12, the optimum reaction temperature was evaluated as -40 °C, where the yield was around 52%.

**Figure 10.** Variation of yield of ADN with time at -40 °C.

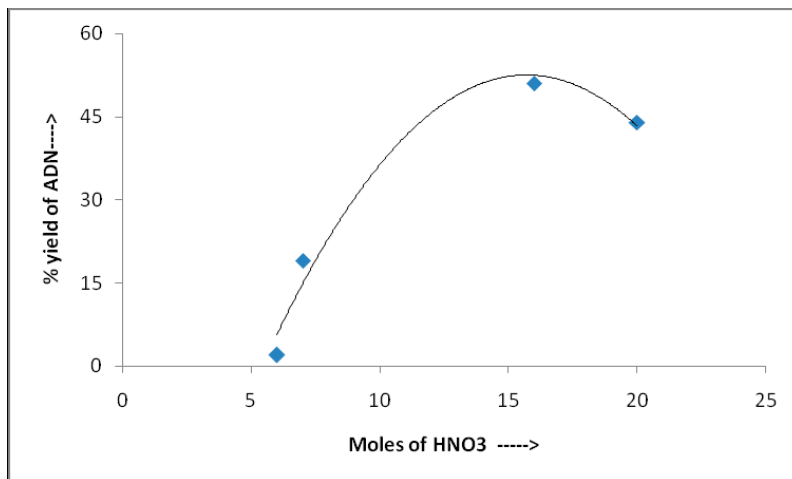


Figure 11. Effect of nitric acid surplus on the yield of ADN.

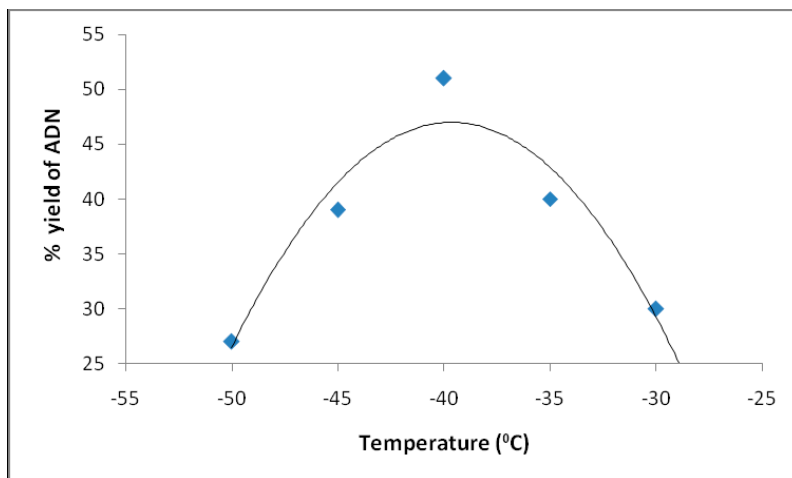


Figure 12. Effect of temperature on yield of ADN.

4 Results and Discussion

The data generated during the various experimental batches for the nitration of AS were used to find the concentration profiles of AS at different times at constant temperature. The variation of concentration with time at -50, -40 and -30 °C are shown in Figures 3-5, respectively. The variation of nitric acid concentration is

shown in Figure 7. It is seen that the change in HNO_3 concentration is almost negligible compared to the concentration changes of AS. So the rate law is evaluated on the basis of the AS concentration. The natural logarithm (\ln) of $\left[-\frac{dC_B}{dt} \right]$ and $\ln(C_B)$ values were tabulated and plotted. Plot of these at -40°C

is shown in Figure 8. Three equations for the rate of reaction obtained at -50 , -40 and -30°C are tabulated in Table 1. It is seen that the order n of reaction is $2.1 \approx 2$ (pseudo 2nd order). Reaction rate constant k , having unit $(\text{mol/L})^{-1} \cdot (\text{min})^{-1}$ increases with increase in temperature from -50 to -40°C . However, it decreases from -40 to -30°C . The value of k is 0.006849 at -50°C , 0.01113 at -40°C , and 0.00607 at -30°C . This indicates that for an increase of temperature of 10°C (from -50 to -40°C), the rate constant increases by 1.62 times, however k decreases by 0.54 times for the same increase in temperature from -40 to -30°C . Using these rate equations, the reaction times for different temperatures can be calculated by common equations (4). It is found that for about 50% conversion of AS to ADN, the required reaction time (min) would be 148, 79 and 131 at -50 , -40 and -30°C , respectively. The temperature dependent rate law corresponding to Eq. (7) is obtained graphically by plotting $\ln(k)$ vs. $1/T$, Figure 9, where the activation energy (E) is about -4.6 kcal and the frequency factor (k_o) ~ 200 . Negative value of the activation energy implies that the reaction rate decreases with increase in temperature as the probability of the colliding molecules reacting with one another in the reaction cross section reduces. Hence, the reaction is essentially required to be operated at the lowest possible optimum operating temperature (*i.e.* here it is -40°C). From Figure 10, it is seen that at -40°C about 52% conversion takes place in 60 min and the yield decreases with increase in time from 60 to 90 min or 120 min, whereas, around 30-34% conversion takes place in the same time at -50°C and at -30°C , respectively. Figure 11 shows the effect of nitric acid on the yield of ADN. Figure 12 describes the effect of temperature on the yield of ADN. The maximum yield was obtained at -40°C . The optimized quantities (g) of the chemicals required for a batch size of 10 g AS are HNO_3 (98%): 88.4, H_2SO_4 (98%): 23.2, ice: 105; rpm of agitator 400.

5 Conclusions

A few of the inferences that may be drawn from the above studies of the kinetics and process optimization are:

- The nitration of AS is a pseudo 2nd order reaction.
- The optimum reaction temperature for the nitration is about -40°C .

- The yields of ADN at -35 °C and -45 °C are less than that at -40 °C.
- The pseudo reaction rate constant is $0.01113 \text{ (mol/L)}^{-1} \cdot \text{(min)}^{-1}$ at -40 °C.
- Using the rate equation, the optimum reaction time is 79 min at -40 °C.
- The activation energy evaluated from the temperature dependent rate equation is -4.6 kcal/mole.
- An increase in temperature of 10 °C (from -50 to -40 °C), causes the reaction rate constant to increase 1.62 times, however, the rate constant decreases by 0.54 times for a similar increase in temperature from -40 to -30 °C.
- The negative value of the activation energy implies that the reaction rate decreases with an increase in temperature.
- The frequency factor calculated for the reaction is 200.

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